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Catalytic oxidative desulfurization of Malaysian diesel utilizing palm kernel shell activated carbon supported cerium/iron oxide

Nurul Syafiqah Mohd Zain, Wan Azelee Wan Abu Bakar*

Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia

**Corresponding author email: wazelee@kimia.fs.utm.my*

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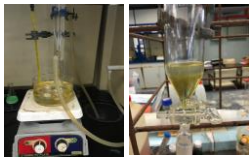
GRAPICAL ABSTRACT



(a) Step of Catalytic Oxidative Desulfurization of Commercial Diesel

ABSTRACT

Existing technique of hydrodesulfurization (HDS) is no longer applicable in achieving Euro IV standard diesel due to the high operational cost, low efficiency and high operating temperature in hydrogen gas atmosphere. Due to these drawbacks, the utilization of the catalytic oxidative desulfurization (CODS) was introduced to complement the HDS process. In this study, the performance of activated carbon supported cerium and iron oxide catalysts were investigated using *tert*-butyl hydroperoxide (TBHP) as oxidizing agent and *N*,*N*-dimethylformamide (DMF) as extraction solvent. The effect of dopant ratio, calcination temperature, number of loading and desulfurization treatments were studied. The results showed that effective dopants ratio (% atomic weight) of Ce/Fe (80:20) prepared by wet impregnation method calcined at 400°C was the best catalyst in this study. Nitrogen adsorption/desorption measurement of CeO_2/Fe_2O_3 (80:20)-AC exhibited the characteristic of microporous structure with Type 1 IUPAC isotherm. The micrograph of the field emission scanning electron microscopy (FESEM) illustrated an inhomogeneous distribution of various particle sizes composed of cerium and iron oxides as been proven by energy dispersive X-ray analysis (EDX) on the surface of prepared bimetallic oxides catalyst. The deep desulfurization of Malaysian commercial diesel fuel contained 440 ppm sulfur was achieved after oxidation with two cycle extraction process with 98% total sulfur removal to produce Green Diesel contained 8.8 ppm sulfur has been measured using GC-FPD. The results obtained has proven that CeO_2/Fe_2O_3 (80:20)-AC can be used as potential catalyst for the removal of sulfur in the Malaysian diesel towards achieving the green diesel production.

Keywords: Catalytic Oxidative Desulfurization, commercial diesel, TBHP, CeO_2/Fe_2O_3-AC, palm kernel shell, activated carbon

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1. INTRODUCTION

Creating a sustainable environment for all the people was the main aims for the entire nation today for the developing country in the past few years to provide a healthy environment for the future generation. One of these green technologies was to produce ultra-low sulfur content in commercial diesel. The existing technique of hydrodesulfurization (HDS) is no longer applicable in achieving Euro IV standard diesel due to the high operational cost, low efficiency and high operating temperature in hydrogen gas atmosphere. Due to these drawbacks, the utilization of other methods such as catalytic oxidative desulfurization (CODS), ionic liquid desulfurization and biodesulfurization were introduced to complement the HDS process [1, 2]. Generally, CODS consists of 2 main steps, oxidation of adsorbed sulfur containing compounds that produce highly polarized sulfones or sulfoxide with the aid of catalyst and oxidizing agent followed by the extraction process using polar solvent.

The selection of the potential catalysts is dependent on their adsorption ability and the common adsorbent used are silica, alumina, zeolite, clay, chitosan and activated carbon (AC). The activated carbon (AC) has been found to be the most possible substitute catalyst to replace chemical supported existing catalyst due to their availability which can be synthesized from variety of sources such as charcoal, wood, sewage sludge and lignocellulosic biomass (palm kernel shell, PKS). The main properties that shown by AC are large specific surface area, high pore volume, well-developed porous structure and high thermal stability. The chemical modification of the adsorbent such as surface impregnation with the active metals and their oxides is necessary depending on the application [3, 4].

The used of AC impregnated with several metal oxides (Ce, Fe, V, Mn) as a sorbent for simultaneous removal of SO_2 and NO gas have been reported by Sumathi *et al*., (2010), [5]. The results showed that AC modified by CeO_2-AC gave the highest sorption capacity at 150°C reaction temperature. The results mainly attributed to the physicochemical properties of CeO_2-AC that enhanced the catalytic activity. Cerium oxide was selected as the metal loading because it has high specific surface area and strong redox ability. It was also possess a higher degree of stabilization upon ionization that a highly basic catalyst like cerium oxide can enhance the CO_2 adsorption and chemisorption on the catalyst surface. Its excellent redox properties resulted in a very fast reduction of Ce^{4+}/Ce^{3+}, which attributed to the formation of oxygen vacancies on the surface [5].

Danmaliki *et al*., (2017), [1] prepared a cerium-loaded AC by thermo co-precipitation method by 10% metal loading and evaluated the efficiency of the catalyst for the removal of thiophene, benzothiophene (BT) and dibenzothiophene (DBT) from model diesel fuel. The study confirmed that cerium loading on the surface of AC enhanced the selectivity and capacity towards thiophenes compared to undoped AC and the improved performance was mainly due to changes in surface chemistry. However, the catalytic activity of desulfurization increased as introducing Fe oxide as bimetallic dopant [1]. In this work, we focused on synthesizing bimetallic catalyst of CeO_2 and Fe_2O_3 with different dopants ratio supported on AC utilized from PKS for desulfurization of commercial diesel by wet impregnation method using *tert*-butyl hydroperoxide (TBHP) as oxidizing agent and *N*,*N*-dimethylformamide (DMF) extraction solvent.

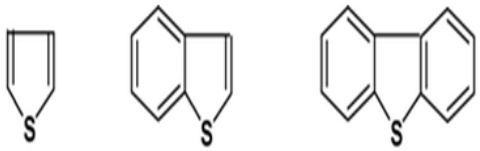

Fig. 1 Chemical structure of a) thiophene, b) BT and c) DBT [6]

2. EXPERIMENTS

2.1 Preparation of AC from PKS

AC was derived from PKS which involved the washing and drying process in oven overnight to remove the impurities. The dried PKS was then treated with 85 wt% phosphoric acid for 20 hour followed by drying in an electrical oven at 110°C overnight. The final step in the preparation of activated carbon is the activation process of catalyst at 500°C in muffle furnace for an hour with a ramp of 5°C min^{-1}. The activated carbon is then continuously washed with distilled until the pH of the solution is close to the initial pH of the rinsing water. Finally, the activated carbon was dried in an electrical oven at 110°C for 24 hour before ready to be used.

2.2 Synthesis of CeO_2-AC, CeO_2/Fe_2O_3-AC Catalysts

Wet-impregnation method was used for synthesis of nanocomposites with 10 wt% metal loading. 10.0 g of AC was impregnated with 3.0990 g of $Ce(NO_3)_3.6\ H_2O$ for CeO_2-AC, 0.8037 g $Fe(NO_3)_3.9H_2O$ for CeO_2/Fe_2O_3 (90:10)-AC, 1.8084g $Fe(NO_3)_3.9H_2O$ for CeO_2/Fe_2O_3 (80:20)-AC and 3.1001g $Fe(NO_3)_3.9H_2O$ for CeO_2/Fe_2O_3 (70:30)-AC respectively. Then, the overnight dried adsorbents were calcined at 400°C and 350°C for an hour to ensure the adequate localization of the matals to the surface of the support and to obtain suitable phase of metal.

2.3 Characterization of catalysts

The surface morphology and particle size of the prepared catalysts were examined using Hitachi SU8020 UHR Cold Emission Scanning Electron Microscopy coupled with EDX. The energy dispesive X-ray spectroscopy (EDX) analysis was employed to obtain the element forming of the prepared catalyst. The porous structure and the Langmuir surface area of the synthesized AC, CeO_2-AC, CeO_2/Fe_2O_3 (80:20)-AC calcined at 350°C and CeO_2/Fe_2O_3 (80:20)-AC calcined at 400°C were characterized using Micromeritics ASAP 2010 volumetric adsorption analyzer at 77K.

2.4 Catalytic oxidative desulfurization experiment.

The catalytic oxidation of commercial diesel was carried out in a round bottom flask, equipped with a magnetic stirrer, a thermometer and a condenser. In a typical run, the paraffin oil bath was first heated and stabilized to 60°C. A mixture of commercial diesel (10 mL, 440 ppm S compounds), TBHP 70% (20 µL, with TBHP/S molar ratio = 3:1) and solid catalyst (0.1 g) was refluxed at 60°C and stirred in 100 mL round bottomed flask for 30 minutes. The flask was set up with a condenser, mechanical stirrer and thermometer under paraffin oil bath. After the completion of oxidation process, the oxidized diesel was extracted by using 10 mL of DMF with ratio diesel to solvent 1:1 for 30 min with continuous stirring. Next, the mixture was separated from the aqueous layer in separating funnel for an hour. Then, the treated diesel was collected in the sample bottle separately for analysis by injecting 1.0 µL of sample to GC-FPD to determine the percentage of sulfur compounds removal after treatment by comparing the total peak area of untreated diesel with the treated one.

2.5 Analysis of treated diesel

The treated diesel fuel was analyzed using Gas Chromatography-Flame Photometric Detector (GC-FPD) to determine the percentage of sulfur reduction from commercial diesel fuel after the treatment. The column that being use was a non-polar column, HP-1 (100% dimethyl polysiloxane, 50 meter length, 0.2 mm internal diameter, 0.5 µm width) the inlet and detection temperature was maintained at 250°C. Helium gas was used as the carrier gas for mobile phase with flow rate of 1.2 mL min^{-1} where required 1.0 µL of sample. The temperature of column oven was programmed with initial temperature maintained at 200°C. The temperature is then increased to 260°C with rate 20°C/min for 10 minutes. At final stage, the temperature was increased from 260°C to 280°C. This temperature was maintained for 10 minutes with rate 5°C/min. The peak areas of commercial diesel before and after treatment were compared.

3. RESULTS AND DISCUSSION

3.1 Characterization of Catalyst

3.1.1 Nitrogen Adsorption Analysis (NA)

The adsorption/desorption patterns to determine the porosity of the synthesized AC, CeO_2-AC and CeO_2/Fe_2O_3-AC calcined at 350°C and 400°C are depicted in Figure 2. All of the catalyst displayed Type 1 IUPAC isotherm indicating that the catalysts were consist of micropores. The Langmuir surface area, pore diameter and pore volume of catalysts are presented in Table 1. In general, the different calcination temperatures and loading of single dopant and bimetallic dopants should give different effects on the physiochemical properties of the catalysts. The activated carbon undoped gave the highest Langmuir surface area and pore volume compared to others. However, the high surface area of activated carbon itself did not give the best desulfurization effect due to unavailability of active sites to enhance the oxidation process of sulfur compounds.

Thus, the potential metal oxide, CeO_2 was introduced. However, 10% cerium loading gave very low Langmuir surface area because cerium particles covered most of the activated carbon pores. Next, Fe was introduced to form bimetallic composite of CeO_2/Fe_2O_3-AC composite to enhance the activity of catalyst. Generally, the loading of metal nanoparticles to AC's surface reduced the overall surface area and pore volume. It is because a significant portion of the AC's surface and its oxygen-containing functional group were linked with the metal nanoparticles [1].

The effect of calcination temperatures of the bimetallic catalysts on the surface area were studied at 350°C and 400°C. Based on the results obtained, the surface area, pore size and pore volume increased as increasing calcination temperature. The results were in agreement with the study conducted by Oschatz *et al.*, (2016), [7] which stated that as increase the calcination temperature of the catalyst, the confinement of the metal particles inside the pores is less, hence reduced the volume of the blocked pores. The nitrogen adsorption followed the following order: AC> CeO_2/Fe_2O_3-AC 400°C> CeO_2/Fe_2O_3-AC 350°C> CeO_2-AC.

3.1.2 Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray (EDX)

The morphology of the synthesized adsorbents was characterized using FESEM/EDX. Figures 3 a, b, c and d illustrate the FESEM micrographs of synthesized catalysts at different calcination temperature with 50 000 times magnification. The presence of open and blind micropores increased the surface area of the activated carbon (Figure 2 a). The second catalyst with monometallic cerium precursors used showed well dispersed nanoparticle size cerium species on the activated carbon surface composed of needle shape of nanosized cerium oxides that cover most of the pores of the support (figure 2 b). For the bimetallic metal doped of cerium and iron with ratio 80:20, the image of micrographs showed the dispersion of two different particle sizes on the support materials. For the bimetallic doped calcined at 400°C (Figure 2 d), the dispersion of small and large sized cerium oxide and iron oxide respectively were more evenly distributed throughout the support surface compared to same catalyst calcined at 350°C (Figure 2 c) which showed agglomeration of spesies and contribute to the instability of the catalyst [8].

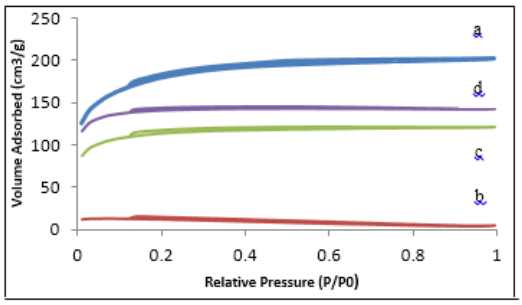

Fig. 2 Isotherm plots of a) AC, b) CeO_2-AC, c) CeO_2/Fe_2O_3-AC 350°C and d) CeO_2/Fe_2O_3-AC 400°C

Table 1 Nitrogen adsorption for activated carbon undoped, monometallic doped and bimetallic doped at different calcination temperatures.

Catalyst	Calcination Temperature (°C)	Surface area (m^2/g)	Average pore size (nm)	Total pore volume (cm^3/g)
AC	-	808	1.9104	0.3130
CeO_2-AC	400	55	0.4639	0.0062
CeO_2/Fe_2O_3-AC	350	525	1.6310	0.1887
CeO_2/Fe_2O_3-AC	400	627	1.7428	0.2206

Table 2 shows the chemical compositions expressed as weight percentage over Ce/Fe (80:20) -AC catalysts calcined at 350°C and 400°C obtained from EDX analysis. The elemental analysis confirmed the presence of C, O, Ce and Fe elements for both catalysts. As shown in the Table 2, the results of the composition elements were differ due to non-homogeneity of the samples throughout the surface respective to the calcination temperature. According to the results obtained, it showed that a huge increase of atomic ratio (%) of C with increasing calcination temperature. This was due to the blocking of the surface of activated carbon support material by the metal oxide particles agglomeration as shown in FESEM micrograph of Figure 2 c and the presence of bulk particles reduced the C contents ratio. For the higher calcination temperature, 400°C, the atomic ratio of the carbon in the surface was 51.8% due to the highly dispersion of metal oxides over the surface of support. In

contrast, it was observed that the compositions of Ce and Fe decreased as the calcination temperature increased. It may have been due to the incorporation of Ce and Fe oxides bulk matrices on the surface of support at lower temperature as can be seen from FESEM micrograph, Figure 2 c [9].

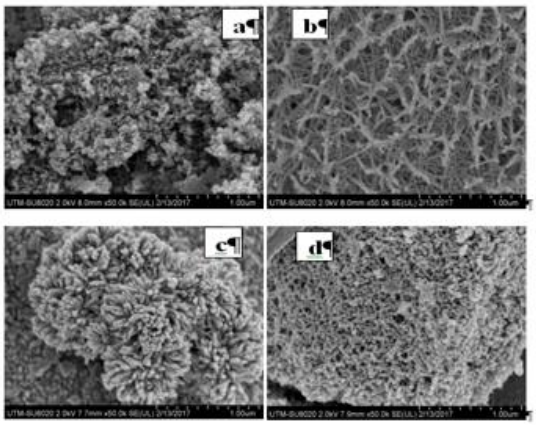

Fig. 3 FESEM micrographs of a) activated carbon support; b) Ce-AC (400°C); c) Ce/Fe (80:20)-AC (350°C), d) Ce/Fe (80:20)-AC (400°C) with scale bar: 1µm, magnification: 50 k

Table 2 EDX analysis for comparison between the elemental compositions of Ce/Fe (80:20) -AC calcined at different temperatures.

Calcination Temperature (°C)	Atomic Ratio (%)			
	C	O	Ce	Fe
350	3.8	36.5	33.1	26.7
400	51.8	39.5	1.4	7.3

3.2 Catalytic Activity Testing

3.2.1 Effect of Dopants Ratio

The effect of dopant ratios of Ce:Fe on the percentage of sulfur removal compounds is given in Figure 4. Based on the results obtained, it could be seen that the activities of the Ce catalyst showed slightly changes after the addition of Fe as bimetallic dopants with the optimum ratio of 80:20 CeO_2/Fe_2O_3-AC compared to single dopant of Ce. The lower percentage of sulfur removal obtained from 90:10 of Ce: Fe loading might due to the insufficient of iron oxide active sites produced. However, the higher loading of Ce: Fe (70:30) reduced the catalytic activities. These results suggested that Fe which acted as a promoter was only required in small quantities. The excessive loading of Fe in the catalyst caused the agglomeration of Fe_2O_3 on the catalyst surface which lowered the dispersion and weaken the catalytic activity [10]. The result on catalytic activity of optimum bimetallic dopants was in agreement with the FESEM micrographs that showed the highly dispersion of metals oxides throughout the support material that produced the higher surface area.

3.2.2 Effect of Calcination Temperature

The difference in calcination temperatures affects the percentage composition of metal oxides on the surface of catalyst. It was observed that the high calcination temperature influenced the distribution of metal oxides on the surface of support. As the temperature increases the metal oxide is more evenly distributed and more effective towards desulfurization of diesel compounds as shown in Figure 5. However, at lower calcination temperature the percentage desulfurization reduced due to the agglomeration of species occurred by the bulk metal oxide particles, hence blocking pores of AC support material that responsible for the adsorption of the sulfur compounds [7].

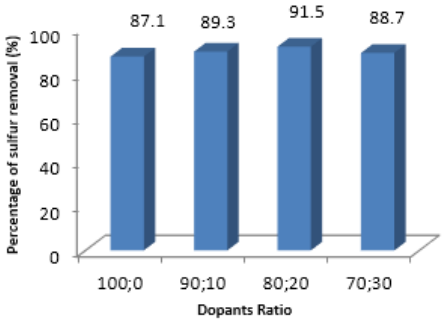

Fig. 4 Effect of dopants ratio; Ce: Fe on the concentration of sulfur remained after treatment. Reaction condition: Diesel= 10 mL, TBHP/S ratio= 3:1, Catalyst loading: 0.1 g, Reaction Time= 30 min, Calcination temperature of catalyst = 400 °C.

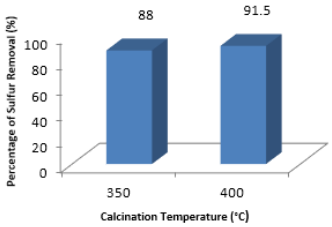

Fig. 5 Effect of calcination temperature of Ce/Fe (80:20)-AC on the percentage of sulfur reduction. Reaction condition: Diesel= 10 mL, TBHP/S ratio= 3:1, Catalyst loading: 0.1 g, Reaction Time= 30 min

3.2.3 Effect of Dosage

The effect of CeO_2/Fe_2O_3-AC dosage on the percentage adsorption of sulfur compounds is given in Figure 6. Determining the optimum dosage of an adsorbent is an important parameter in adsorption studies, and the dosage of 0.1-0.4 g catalyst loading was investigated. The highest percentage of sulfur removal was observed in the system catalyzed by 0.1 g of catalyst in 10 mL diesel with 86.2% reduction to produce the treated diesel with only contained 60.8 ppm sulfur after treatment. According to the results, the increase in loading of catalyst does not affect the sulfur removal efficiency of the commercial diesel. This was probably due to the catalyst has reached it maximum catalyst loading for the reaction. This phenomenon is due to the effect where some of the catalyst may become the reactant

and undergo reaction process and deactivate themselves, hence reduced the number of active catalyst. Thus, the catalytic activity of catalyst decreased and became constant as the catalyst loading increased [11].

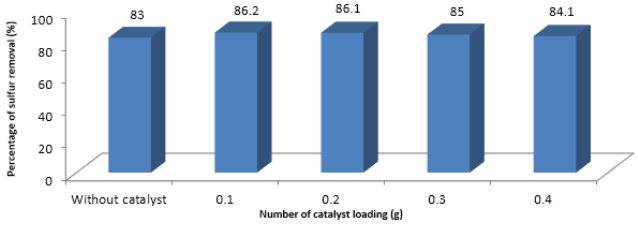

Fig. 6 Effect of number of loading; Ce/Fe (80:20) -AC on the percentage of sulfur reduction. Reaction condition: Diesel= 10 mL, TBHP/S ratio= 3:1, Catalyst loading: 0.1 g, Reaction Time= 30 min, Calcination temperature of catalyst = 400 °C.

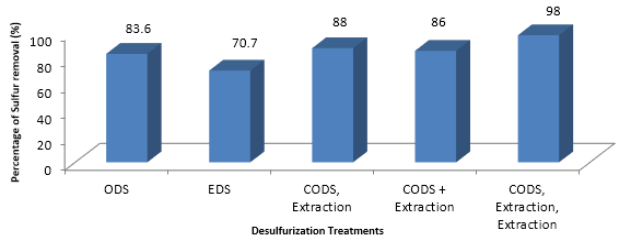

Fig. 7 Effect on series of desulfurization treatments on the concentration of sulfur remained (ppm). Reaction condition: Diesel= 10 mL, TBHP/S ratio= 3:1, Catalyst loading: 0.1 g of Ce/Fe (80:20) -AC, Reaction Time= 30 min, Calcination temperature of catalyst = 400°C.

3.2.4 Effect on Desulfurization Treatments

The experiments were carried out to study the removal of sulfur compounds from commercial diesel with different desulfurization treatments as shown in Figure 7. The performance of ODS process were compared with the EDS (desulfurization without catalyst) process. The total sulfur removal efficiencies using EDS and proposed ODS processes were about 70.7 and 83.6% respectively from the original concentration, 440 ppm. The low efficiency of EDS process was probably due to the low polarity of sulfur compounds which lowered its affinity towards the polar solvent in diesel phase [12]. According to the results obtained, it is interesting to note that after employing the catalyst, the sulfur removal performance of ODS process achieved 88% sulfur reduction with a single extraction step. Nevertheless, the desulfurization efficiency diminished when the extraction was coupled with oxidation in a single pot. This was probably due to fact that the extractant solvent may deactivate the catalyst, thus inhibiting the surface reaction of the catalyst. It was suggested that the single extraction was insufficient to remove sulfones or sulfoxides and that two successive extractions would produce better results. The optimum desulfurization of diesel fuel can be achieved by CODS and followed by double extraction that able to produce green diesel (Euro V) which only contained 8.8ppm sulfur compounds by 98% sulfur reduction. Therefore, CODS followed by double solvent extraction was adopted in this study.

4. CONCLUSION

In this study, the research focused on removal of sulfur compounds in commercial diesel fuel by using bimetallic composite supported on the activated carbon catalyst utilized from agricultural waste, palm kernel shell. Meanwhile, the bimetallic catalysts were synthesized by using cerium and iron with different dopants ratio and calcination temperatures to enhance the activity of the catalysts. The potential catalysts from screening process monitored by GC-FPD were then optimized according to the various number of loading and desulfurization treatments. It is possible to reduce the sulfur content in commercial diesel from 440 ppm up to 8.8 ppm sulfur under mild condition using the best catalyst CeO_2/Fe_2O_3 (80:20)-AC calcined at 400°C with 10 g/L catalyst loading with percentage reduction of 98% after CODS and double extraction process. FESEM micrograph results showed that the catalyst, CeO_2/Fe_2O_3 (80:20)-AC calcined at 400°C produced highly dispersion of CeO_2 and Fe_2O_3 nanoparticles on the surface. The results obtained from EDX analysis confirmed the presence of Ce and Fe metal on the activated carbon support. NA analysis revealed the catalyst exhibit the isotherm Type 1 indicating the presence of micropores. The results may indicate that activated supported cerium and iron based catalyst has the potential to be used as catalyst in CODS to meet the future regulation of sulfur in diesel fuel. The catalyst and CODS with double extraction method can be used to treat commercial diesel to achieve green diesel in the future.

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